

PATENT SPECIFICATION

873,067

NO DRAWINGS.

Inventors:—DEREK SOUTHERN, CHARLES BUCHAN MILNE
and GERALD ROBINSON.



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and 91, F(1:2).

International Classification:—C08f. G10m.

COMPLETE SPECIFICATION.

ERRATUM

SPECIFICATION NO. 873,067

Page 1, in the heading International Classification for "G10m" read "C10m"

THE PATENT OFFICE,

25th August, 1961.

method by which it is to be performed,
to be particularly described in and by the
following statement:—

10 The present invention relates to the pre-
paration of hydrocarbon polymers suitable
for use as synthetic lubricating oils and
viscosity index improvers.

15 It has recently been discovered that such
polymers can be produced from certain
olefines and by using catalysts of specified
composition as described in the Specifica-
tions of co-pending Applications 27,109/57
(Serial No. 824,460), 752/59 cognated with
12607/59 (Serial No. 873,064), and 4774/59
20 (Serial No. 873,065).

According to the present invention poly-
mers of improved colour, reduced sulphur
content and having greater antioxidant
susceptibility are produced by a process in
25 which an olefine having in the molecule at
least six but not more than twenty-five and
preferably not more than eighteen carbon
atoms is polymerised in the presence of a
catalyst comprising Components A and B
30 (as hereinafter defined) and the polymer is
treated with hydrogen in the presence of a
hydrogenation catalyst.

By virtue of the work originated by K.
Ziegler the catalyst used is usually referred
35 to as a Ziegler catalyst and the co-polymer-
isation process as the "Ziegler process".
As indicated for example in Patent Speci-
fications Nos. 799,392, 799,823 and 801,031
and in the Specifications of Patent Applica-

DS 95874/1(18)/R.153 200 8/61 PL
the catalyst used in this specification is
formed therefore by mixing at least one
Component A with at least one Component B
as defined below. If desired, for example
when using high catalyst mole ratios (B:A),
other compounds, for example molecular
weight modifiers, which are capable of
influencing the polymerisation process may
be used in addition. Some suitable mole-
cular weight modifiers, for example Lewis
bases, hydrogen active compounds and BF₃,
55 are described in the Application Nos.
23,906/56, 23907/56 and 35,963/56 (Serial
Nos. 851,113, 851,112, 851,119).

In this Specification Component A is
defined as a compound (preferably other than
a heat-treated oxide, a carbide, or a naturally-
occurring compound), of a metal of Groups
4a, 5a, 6a, 7a or 8 of the Periodic Classifica-
tion of Elements, although the compound is
more suitably an inorganic compound for
example a halide, or oxyhalide of Groups 4a,
5a or 6a. It is preferred however, that
Component A should comprise a chloride,
bromide or iodide of a Group 4a or 5a metal
particularly that of titanium, zirconium or
vanadium. The most preferred compound is
titanium tetrachloride, although the higher
chlorides of, for example, zirconium and
vanadium can be used.

When producing polymers suitable as
lubricating oils with a catalyst component
mole ratio of less than 1:1 it is also prefer-
able that the compounds which are used as

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and 91, F(1:2).

International Classification:—C08L G10m.

COMPLETE SPECIFICATION.

Hydrocarbon Polymers.

We, "SHELL" RESEARCH LIMITED, a British Company, of St. Helen's Court, Great St. Helen's, London, E.C.3, do hereby declare the invention, for which we pray that

a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of hydrocarbon polymers suitable for use as synthetic lubricating oils and viscosity index improvers.

It has recently been discovered that such polymers can be produced from certain olefines and by using catalysts of specified composition as described in the Specifications of co-pending Applications 27,109/57 (Serial No. 824,460), 752/59 cognated with 12607/59 (Serial No. 873,064), and 4774/59 (Serial No. 873,065).

According to the present invention polymers of improved colour, reduced sulphur content and having greater antioxidant susceptibility are produced by a process in which an olefine having in the molecule at least six but not more than twenty-five and preferably not more than eighteen carbon atoms is polymerised in the presence of a catalyst comprising Components A and B (as hereinafter defined) and the polymer is treated with hydrogen in the presence of a hydrogenation catalyst.

By virtue of the work originated by K. Ziegler the catalyst used is usually referred to as a Ziegler catalyst and the co-polymerisation process as the "Ziegler process". As indicated for example in Patent Specifications Nos. 799,392, 799,823 and 801,031 and in the Specifications of Patent Applica-

tions Nos. 23231/55, 23501/55 and 16362/55 (Serial Nos. 820,263, 819,867, 810,023), the Ziegler process is carried out using at least two components which may be referred to as Components A and B.

The catalyst used in this Specification is formed therefore by mixing at least one Component A with at least one Component B as defined below. If desired, for example when using high catalyst mole ratios (B:A), other compounds, for example molecular weight modifiers, which are capable of influencing the polymerisation process may be used in addition. Some suitable molecular weight modifiers, for example Lewis bases, hydrogen active compounds and BF₃ are described in the Application Nos. 23,906/56, 23907/56 and 35,963/56 (Serial Nos. 851,113, 851,112, 851,119).

In this Specification Component A is defined as a compound (preferably other than a heat-treated oxide, a carbide, or a naturally-occurring compound), of a metal of Groups 4a, 5a, 6a, 7a or 8 of the Periodic Classification of Elements, although the compound is more suitably an inorganic compound for example a halide, or oxyhalide of Groups 4a, 5a or 6a. It is preferred however, that Component A should comprise a chloride, bromide or iodide of a Group 4a or 5a metal particularly that of titanium, zirconium or vanadium. The most preferred compound is titanium tetrachloride, although the higher chlorides of, for example, zirconium and vanadium can be used.

When producing polymers suitable as lubricating oils with a catalyst component mole ratio of less than 1:1 it is also preferable that the compounds which are used as

Component A are ones which are liquid at normal temperatures and pressures and ones in which the metal present in the compound is in its highest valency state.

5 Component B is defined as an element or compound of either of the following :—

- (1) A group I metal or an alloy thereof, or
- (2) An organo-metallic compound or a hydride of a Group 1, 2 or 3 metal, tin or lead.

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The term "organo-metallic compound" means a compound (other than an inorganic metal carbide) in which the metal is directly attached to a carbon atom, for example, zinc dimethyl, magnesium dipropyl. The organo-metallic compound or hydride may for example be a molecular compound with an ether, or amine or a complex compound with an alkali metal hydride, alkali metal alkyl, alkali metal aryl or alkali metal halide, for example lithium aluminium hydride and sodium aluminium triethyl chloride.

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It is preferable however that Component B should comprise either :—

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- (1) An aluminium trialkyl ; or
- (2) An aluminium compound of the general formula R_1R_2AlX in which R_1 and R_2 are similar or dissimilar and each represents a hydrogen atom or a hydrocarbon radical such as an alkyl, alkaryl, aryl, aralkyl, alkenyl, alkynyl, cycloalkyl or cycloalkenyl radical and X represents a hydrogen atom, a halogen atom, an alkoxy group or an aryloxy group or the residue of a secondary amine or amide, carboxylic acid or sulphonic acid ; or
- (3) An aluminium compound of the general formula $RAlX_1X_2$ in which R represents a hydrogen atom or a hydrocarbon radical as in (2) above, and X_1 and X_2 are similar or dissimilar and each represents a halogen atom, an alkoxy group or an aryloxy group.

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Examples of such aluminium compounds are :—aluminium triethyl, diethyl aluminium bromide, dimethyl aluminium hydride, phenoxydiethyl aluminium, dimethylaminodiethyl aluminium, piperidyl diethyl aluminium, (methylcyclohexylamino) - diethyl aluminium, (N - methylamine) - diethyl aluminium, diisobutyl aluminium benzoate, ethyl aluminium dichloride, and diethoxyethyl aluminium.

The most preferred aluminium compounds are those in which the alkyl group has less than six carbon atoms, for example aluminium triethyl or aluminium diethyl chloride or bromide, the particularly preferred compound being aluminium triethyl, although aluminium triisobutyl can be used.

The process of the present invention is particularly applicable to those olefines obtained by the thermal or catalytic cracking of hydrocarbon feedstock, such as that produced in the refining of crude petroleum 65 petroleum oils. Such olefines that are commonly known as cracked wax olefines are particularly preferred. Other preferred olefines are those known as cracked raffinate olefines which are obtained from the cracking 70 of the raffinate or furfural extraction of heavy catalytically cracked cycle oil. Both cracked wax olefines and cracked raffinate olefines can be fractionally distilled to obtain the cuts containing the individual 75 olefines.

Other olefines which can be used are those produced by the polymerisation of lower molecular weight olefines, for example propylene or butylene or mixtures of propylene 80 and butylene. They may also, for example, be those obtained by the dehydration of suitable alcohols or alcohol mixtures.

The process of the present invention is suitable not only for olefines having the same number of carbon atoms in the molecule, but is also suitable for mixtures of such olefines, for example mixtures of C_6 to C_8 , C_9 to C_{13} , C_9 to C_{17} , and C_{14} to C_{18} olefines. Particularly preferred mixtures of olefines 90 are cracked wax olefines and cracked raffinate olefines.

In general, the preferred olefines are those olefines or mixtures of olefines consisting entirely of straight-chain alpha olefines or a large proportion of such olefines. For the production of polymers suitable as lubricating oils using a low catalyst component (B : A) mole ratio i.e. less than 1 : 1, particularly not more than 0.6 : 1, it is also 100 possible to use olefines or mixtures containing a large proportion of olefines of the

general formula
$$\begin{matrix} R \\ > \\ R_1 \end{matrix} C = CH_2$$
 wherein R and R_1 are similar or dissimilar alkyl groups.

To obtain a better polymerisation reaction 105 and a good yield of polymer it is preferable that the olefine should be purified before polymerising in the presence of the catalyst. One such method is purification using one of the catalyst components, for example treatment with a solution of titanium tetrachloride in which the precipitate formed on adding titanium tetrachloride to the olefine is removed by filtration. The filtrate is 110 when washed successively with a dilute solution of hydrochloric acid, for example a 16% solution, and aqueous sodium carbonate, for example 5%, and then distilled water. The olefine is then distilled from 115 sodium.

In another method of purification, that is with sulphuric acid, the olefine, preferably after being deperoxidised by agitation with 120

an acidified aqueous solution of ferrous sulphate, is cooled to and maintained at a temperature below 10° C., and concentrated sulphuric acid, for example 96%, is added dropwise to the vigorously agitated olefine. After removing the acid sludge layer more concentrated sulphuric acid is added under similar conditions. This procedure is repeated once more and after the third extraction the olefine is washed with water, dilute aqueous sodium hydroxide, for example 4%, and then water until neutral. The olefine is then treated with a drying agent, for example calcium chloride or dried, for example by the use of molecular sieves, and then distilled under a reduced pressure of about 1 mm. mercury from sodium.

It is also possible to continue the purification treatments, e.g. by washing with sulphuric acid followed by treatment with titanium tetrachloride.

For straight-chain alpha olefines or mixtures containing a large proportion of straight-chain olefines it is preferable that the olefine be purified by treatment with urea as described in the Specification of our co-pending Application 4774/59 (Serial No. 873,065). Thus, the olefine or olefine mixture is treated with urea, preferably in aqueous, alcoholic or aqueous-alcoholic solution to form a slurry or complex comprising the adduct. In a preferred modification the adduct is formed and separated in the presence of a wetting agent, for example sodium alkyl sulphates having from eight to nineteen carbon atoms in the alkyl group, and preferably water-soluble salts, for example ammonium salts, particularly ammonium carbonate, and potassium carbonate. After separation of the top layer of unreacted raffinate hydrocarbon by gravity the adduct can be decomposed by heating to between 70° and 75° C. to yield as upper layer the purified olefine or olefine mixture. However, according to the preferred embodiment of the purification by urea extraction, the adduct slurry (after removal of the raffinate hydrocarbon by separation under gravity) is stirred and washed with a solvent substantially immiscible in water such as toluene. After settling the adduct slurry is separated from the toluene phase and decomposed by heating to between 70° and 75° C. as before.

After purification by urea extraction the olefine can be further treated, for example by distillation over sodium, treatment with small quantities of one of the catalyst components, e.g. titanium tetrachloride or triethyl aluminium, or purification by treatment with sulphuric acid.

After purification the olefine may be washed with water and dried, for example over calcium chloride, or over molecular sieves.

Although the olefines purified by any one

of the methods hereinbefore described are readily polymerisable according to the process of the invention it has been found that further purification by silica gel improves the yield of polymer. Accordingly, the olefine, purified by any of the above described methods, and dried, is preferably further purified by percolation through activated silica-gel, for example by allowing the olefine to pass through a column containing granules of silica-gel. The olefines can then be dried, for example over molecular sieves.

The polymerisation is most conveniently carried out in a solvent, the solvent being substantially inert under the reaction conditions. Suitable solvents include saturated aliphatic hydrocarbons which are liquid under reaction conditions, for example, *n*-hexane, *n*-pentane, iso-octane, and *n*-decane and aliphatic or substantially aliphatic petroleum spirits. The preferred solvents are iso-octane and cyclohexane.

In carrying out the reaction using this type of catalyst system an inert atmosphere in the reaction vessel is essential, otherwise the Component B may decompose, reacting violently. Accordingly, before adding the olefine and solvent to the reaction vessel an inert atmosphere is created by purging the vessel with a dry inert gas, for example nitrogen. The catalyst components dissolved in the inert solvent are then introduced into the vessel.

It has been found that a concentration of catalyst to olefine, such that the mole ratio of Component A, for example titanium tetrachloride, to olefine lies between 0.005 : 1 and 0.1 : 1, preferably between 0.015 : 1 and 0.04 : 1, is very suitable. When mixtures of olefines containing olefines having different numbers of carbon atoms in the molecule are used it is to be understood that the molecular weight of the olefine is the theoretical mean molecular weight of the mixture.

Although the mole ratio of Component B to Component A can be varied over a wide range it is desirable that the mole ratio (B : A) should be at least 0.05 : 1 and not more than 20 : 1.

When producing polymers which can be used as lubricating oils, it is essential that the mole ratio (B : A) be less than 1 : 1 and preferably between 0.05 : 1 and 0.9 : 1. With olefines or mixtures containing a large proportion of olefines having the general

formula
$$\begin{matrix} R \\ \diagup \\ C=CH_2 \\ \diagdown \\ R_1 \end{matrix}$$
 it is preferable that the

mole ratio of compounds B : A should be between 0.05 : 1 and 0.6 : 1 for at higher catalyst mole ratios in some cases very little polymerisation occurs with such olefines. It is also preferable both for straight- and branched chain alpha olefines that the

monomer should not contain more than eighteen carbon atoms in the molecule.

A particular advantage of the polymers produced according to the process of the present invention which can be used as lubricating oils *per se* is that at low temperatures, for example below 0° F., their viscosity does rise rapidly as the temperature is reduced and is appreciably lower therefore than, for example, that of polyoxyalkylene fluids or of mineral oils having a similar viscosity at normal temperatures.

When producing polymers especially from straight-chain alpha olefines or mixtures containing a large proportion of such olefines and using catalyst component mole ratios (B : A) of less than 1 : 1 it is preferable to use lower catalyst component mole ratios for the higher olefines and higher mole ratios for the lower olefines. Thus, for example, for olefines having at least six but not more than eight carbon atoms in the molecule the mole ratio should preferably be between 0.1 : 1 and 0.9 : 1. For olefines having at least nine but not more than thirteen carbon atoms in the molecule a mole ratio of between 0.05 : 1 and 0.7 : 1 is preferred, whilst for tetradecene and higher olefines a mole ratio between 0.05 : 1 and 0.5 : 1 is preferred. The same principle applies for mixtures of olefines.

Polymers which are suitable as viscosity index improvers can also be produced according to the process of the invention. To obtain such polymers, it is preferable to use straight-chain alpha olefines and during the polymerisation to use catalyst component mole ratios (B : A) of at least 1 : 1 and preferably between 1 : 1 and 3 : 1. Higher mole ratios, for example an Al : Ti mole ratio of 8 : 1 can be used, but increasing the mole ratio above about 3 : 1 does not usually have much effect on the polymer properties and may sometimes result in a much reduced yield.

After completion of the reaction, the polymer is treated to inactivate the catalyst and remove the catalyst residues. The inactivation of the catalyst can be accomplished by washing with an alcohol, water or other suitable material, for example methanol, isopropanol or mixtures thereof. Sometimes, the catalyst inactivating treatment also removes a major proportion of the catalyst residues, but usually it is necessary to remove the catalyst residues by treating the polymer with an acid, base or other material, for example dilute hydrochloric acid followed by sodium carbonate solution.

The polymerisation reaction can be carried out as a batch process or it can be adapted to the steady-stage process. In this latter process a polymerisation mixture of constant composition is continuously introduced into the reaction zone and the reaction mix-

ture resulting from the polymerisation is continuously withdrawn in amounts equivalent to the rate of introduction of reactants.

After the polymer has been treated to inactivate the catalyst and the catalyst residues removed, it may be separated from the diluent, for example by distillation. However, as the treatment with hydrogen can be conveniently carried out with the polymer dissolved in the diluent, this separation is unnecessary.

According to the process of the present invention therefore, the polymer, preferably in the presence of diluent, is treated with hydrogen in the presence of a hydrogenation catalyst.

Although any gas mixture can be used containing at least about 50% by weight of hydrogen the remainder being substantially inert it is preferable that reasonably pure hydrogen, for example at least 95% by weight be used.

Although the treatment with hydrogen can be carried out at atmospheric pressure, in order to obtain a more rapid rate of reaction elevated pressures should preferably be used, for example from 10 to 50 atmospheres, although higher pressures, for example 100 atmospheres may be used, if desired.

The treatment with hydrogen is preferably carried out at elevated temperatures, for example, above 50° C., the preferred range being 100° to 200° C. With such elevated pressures and temperatures the reaction should be completed relatively rapidly, for example in under 10 hours.

Many hydrogenation catalysts can be used according to the process of the present invention, for example, powdered nickel, copper chromite, cobalt molybdate, molybdenum sulphide, Raney cobalt, nickel oxide on majolica, copper chromite on majolica and palladised charcoal. The preferred catalyst however, is Raney nickel.

After the hydrogen treatment is complete the solution is filtered and the diluent, if any, removed by distillation.

Sometimes, it may prove desirable or necessary to repeat the above described treatment with hydrogen in the presence of a catalyst on a polymer which has already been treated with hydrogen. Although similar reaction conditions to those used in the first treatment with hydrogen may be used, it is found desirable if a high temperature, for example about 200° C., a low pressure, for example about 50 atmospheres, and a long reaction time, for example about 16 hours, be used. Alternatively, a high temperature, for example about 200° C., a high pressure, for example about 140 atmospheres and a short reaction time, for example about 5 hours, may be used.

Although treatment with hydrogen reduces the sulphur content, improves the

colour and greatly improves the antioxidant susceptibility of the polymer it does however, particularly with polymers suitable as lubricating oils increase the pour point, sometimes by as much as about 100° F.

This disadvantage can be overcome by the removal of the dimer and if necessary other low molecular weight polymer for example by distillation under reduced pressure and accordingly, removal of such polymers is a preferred feature of the present invention, especially when producing polymers suitable as lubricating oils.

The preferred method of removing the dimer and other low molecular weight polymer is by fractional distillation under reduced pressure and is described in the Specification of our co-pending Application 752/59 cognated with 12607/59 (Serial No. 873,064). The low boiling fraction comprising the dimer and in some cases other low molecular weight polymer is removed leaving the desired hydrogen treated polymer as residue.

Although in this manner, the dimer and other low molecular weight polymer can be conveniently removed after treatment with hydrogen it is also quite possible and in some cases preferable, to remove them before treatment with hydrogen. In this case, they are conveniently removed after first distilling off the diluent used in the polymerisation reaction.

In both cases, removal of dimer and other low molecular weight polymer from the polymers suitable as lubricating oils either before or after treatment with hydrogen generally results in a polymer with an acceptably low pour point.

Whilst the polymers produced by the process of the present invention using low catalyst ratios, that is less than 1:1 are satisfactory as lubricating oils *per se* they may of course, be blended with any other natural or synthetic oil having lubricating properties. Such oils may be for example a hydrocarbon oil obtained from a paraffinic, naphthenic, Mid-Continent or Coastal Stock or mixtures thereof.

The polymers may also be blended with synthetic lubricating oils, for example copolymers of alkylene glycols and alkylene oxides; organic esters, e.g. di-(2-ethyl-hexyl)sebacate, dinonyl sebacate, dinonyl adipate, dioctyl phthalate and tricetyl phosphate; polymeric tetrahydrofuran and polyalkyl silicone polymers, e.g. dimethyl silicone polymer.

Whilst the polymers of the present invention are preferably blended with only synthetic lubricating oils, especially diester or polyoxyalkylene lubricating oils, the final blend may comprise any number of suitable oils having lubricating properties.

For certain applications, polymers pro-

duced by the process of the present invention or blends of such polymers with oils having lubricating properties require the addition of additives such as pour point depressors, viscosity index improvers, thickeners, antioxidants, anti-corrosive agents and anti-lacquering agents.

Suitable additives which function as pour point depressors and viscosity index improvers include polymers of esters of acrylic acid or a 2-alkylacrylic acid, for example, the polymers of the methyl, ethyl, *n*-propyl, isopropyl, isobutyl, lauryl, phenyl, or benzyl esters.

Suitable anti-lacquering agents for addition to the polymers produced by the process of the present invention are the salts of aromatic carboxylic acids or of phenols with a metal of Group II of the Periodic Table, which salts are soluble in the synthetic oil. Examples of such salts include the zinc and calcium salts of benzoic acid, naphthenic acid, phenol, the higher alkylate phenols and higher alkylated salicylic acids.

Where a high load carrying capacity is required an extreme pressure additive may be added to the polymers of the present invention. A good type of extreme pressure additive is the trialkyl, triaryl or trialkaryl phosphates, for example trioctyl or tricresyl phosphates.

Antioxidants, for example the alkylated phenols and diphenols and phenothiazine and its alkyl or aryl alkyl substitution products, for example 10-benzyl phenothiazine may also be added to the polymers of the present invention. It is found that the resulting lubricating oil has great oxidation stability.

The polymers produced by using a catalyst mole ratio B:A of at least 1:1 which can be used as V.I. improvers are suitably blended with any mineral, or synthetic lubricating oil. Examples of synthetic oils have already been described and include the polymers produced by the process of the present invention.

The proportion of V.I. improver in the lubricating oil is preferably from 0.1% to 20% by weight and more preferably between 1% and 5% by weight.

In the following examples the relationship between parts by weight and parts by volume is the same as that between the gram and the cubic centimetre.

EXAMPLE I.

A C₃ urea-extracted cracked wax olefine further purified by washing with sulphuric acid, was polymerised using a catalyst mole ratio, triethyl aluminium:titanium tetrachloride of 2:1. The reaction vessel was purged by passing nitrogen into the vessel. 3,300 parts by volume of sodium dried isooctane followed by 13.5 parts by volume of titanium tetrachloride were introduced into

- the vessel and the temperature raised to 40° C., 33.5 parts by volume of triethylaluminium in 100 parts by volume of isooctane, was added and the mixture stirred for 30 minutes. 1000 parts by weight of the olefine was added over a period of one hour and the solution was stirred for a further 22 hours at ambient temperature.
- The catalyst was decomposed by a dropwise addition of a 1 : 1 mixture of isopropanol and methanol (100 parts by volume) and the solution shaken with 16% hydrochloric acid
- until all traces of colour had been removed, followed by washing with aqueous sodium carbonate and water. The solution was dired by entrainment distillation in the presence of benzene (400 parts by volume) and part of the solvent was removed by distillation.
- The polymer solution was divided into three parts and each part was treated with substantially pure hydrogen using different catalysts under the following conditions :—

	Catalyst	Temperature	Pressure	Time
25	(1) 50 parts by weight NiO on majolica	150° to 215° C.	100 atmospheres	3 hours
	(2) 20 parts by weight copper chromite on majolica	150° to 215° C.	100 atmospheres	4 hours
	(3) 60 parts by weight palladised charcoal	150° to 215° C.	100 atmospheres	3 hours

- After the treatment with hydrogen the solutions were filtered in the presence of Clarcel using a filter and the hydrogen treated polymer was isolated. The products were found to be of better colour than the untreated polymer, being either colourless or of only faint colour.
- When blended in a proportion of 4% by weight in Cardon HVI 65 the following viscometric properties were obtained :—
- tetrachloride were injected into a large vessel purged with nitrogen and containing 300 parts by volume of cyclohexane and 300 parts by weight of the olefine. The polymerisation was carried out at 150° C. for 22 hours, the catalyst decomposed and the product treated by the procedure of Example I to yield about 245 parts by weight of polymer (82%).

	Vk _{100° F} CS	Vk _{210° F} CS	K.V.I.
(1)	182.7	23.3	132
(2)	112.7	19.8	145
(3)	135.2	20.3	138

- The corresponding figures for the Cardon HVI 65 base oil are :—

Vk _{100° F.}	31.88 CS	KVI : 100
Vk _{210° F.}	5.17 CS	

- When blended in a proportion of 4% by weight in a synthetic lubricant base the VI properties were also improved.

- When a minor proportion of ionol was added as antioxidant to the blends they were found to have better resistance to oxidation than similar blends with untreated polymers as the V.I. improvers.

EXAMPLE II.

- A purified C₁₀ urea-extract cracked-wax olefine was polymerised using a component mole ratio, triethylaluminium : titanium tetrachloride of 1 : 1. 15 parts by volume of titanium tetrachloride in cyclohexane followed by 12 parts by volume of titanium

When blended as 4% by weight in Cardon HVI 65 as base oil the following viscometric properties were obtained :—

Vk _{100° F.}	63.8 CS
Vk _{210° F.}	10.4 CS
KVI	139

This polymer was tested for its oxidation stability by heating it at 150° C. in an atmosphere of oxygen in the presence of 100 parts per million of copper powder as catalyst. The number of hours T_{6.50} and T₁₀₀₀, required for 100 parts by weight of polymer to absorb 650 or 1000 parts by volume of oxygen respectively were determined. The test was repeated in the presence of 0.73% 10-benzylphenothiazine as antioxidant.

The result obtained were as follows :—

	$T_{0.50}$ (hours)	T_{1000} (hours)
Polymer alone	2	3
Polymer with antioxidant	65	113

- 5 In the presence of antioxidant the values obtained were about 50% greater than the corresponding results obtained when using a polymer which had not been treated with hydrogen.

10 EXAMPLE III.

- A polymer suitable as a lubricating oil was prepared using a catalyst component mole ratio triethylaluminium : titanium tetrachloride of 0.5 : 1. The monomer was an urea-extract C_9 cracked-wax olefine and the polymerisation procedure was similar to that of Example I.

- 20 The solvent and unreacted monomer were removed by distillation under reduced pressure and an 85% yield of polymer, pale yellow in colour was obtained.

- 25 2260 parts by weight of polymer were dissolved in 2,000 parts by volume of cyclohexane, and the solution divided into two portions which were treated with substantially pure hydrogen separately in an autoclave at 190° C. for 10 hours at elevated pressure in the presence of Raney nickel. The solution was filtered, the solvent was removed by distillation, and the treatment with hydrogen repeated using a freshly prepared sample of Raney nickel.

- 30 The product after treatment with hydrogen was filtered and the solvent removed by distillation and it was found that much of

the colour had been removed during the treatment with hydrogen. The product was subjected to vacuum distillation and a fraction boiling between 135° and 162° C. under 0.5 mm. Hg pressure was collected, this residue comprising hydrogen treated polymer was almost colourless while the separated dimer was pale yellow.

The viscometric properties of the hydrogen treated dimer-free polymer were :—

$Vk_{100^\circ F.}$	206
$Vk_{210^\circ F.}$	30.2
KVI	138

The pour point of the dimer-free polymer was -35° C. compared with 20° F. before removal of dimer.

The polymer was found to be much more stable to oxidation compared with polymers produced by similar procedure but which had not been treated with hydrogen.

EXAMPLE IV.

A C_9 urea-extract cracked-wax olefine was polymerised using triethyl aluminium and titanium tetrachloride in mole ratios of 0.3 : 1 and 0.2 : 1 by the procedure of Example I.

The polymers were treated with hydrogen at 190° C. and under pressure for 5 hours over Raney nickel and it was found that the pour points 21° F. and 29° F. respectively had risen by about 100° F. as compared with those before treatment with hydrogen.

The viscometric properties were :—

	Component Mole ratio Al : Ti	$Vk_{100^\circ F.}$	$Vk_{210^\circ F.}$	KVI
(1)	0.3 : 1	45.1	8.2	144
(2)	0.2 : 1	48.7	9.7	>150

- 75 The polymer (1) produced using a 0.3 : 1 mole component ratio was then distilled under reduced pressure to remove the dimer and it was found that the pour point decreased from 21° F. to -74° F. The viscometric properties were :—

$Vk_{100^\circ F.}$ (CS)	82.8
$Vk_{210^\circ F.}$ (CS)	12.2
KVI	133

- 85 The polymers obtained were suitable as lubricating oils and showed good oxidation stability when a minor proportion of antioxidant was blended with them.

EXAMPLE V.

- 90 A C_9 urea-extract cracked-wax olefine was polymerised by the procedure of Example IV using a catalyst component mole ratio (Al : Ti) of 0.3 : 1.

After polymerisation the dimer was removed by fractional distillation under reduced pressure and the dimer-free polymer then treated with hydrogen by the procedure of Example IV. The pour point was -70° F. and the viscometric properties obtained were :—

$Vk_{100^\circ F.}$ (CS)	93.0
$Vk_{210^\circ F.}$ (CS)	13.4
KVI	133

This polymer was found to be suitable as a lubricating oil and showed good oxidation stability when blended with a minor proportion of an antioxidant.

EXAMPLE VI.

Mixtures of C_8/C_9 and C_9/C_{10} urea-extract cracked-wax olefines were polymerised using catalyst component mole ratio, aluminium

triethyl : titanium tetrachloride of 0.3 : 1 and 0.15 : 1 respectively and treated with hydrogen by the procedure of Example II using Raney nickel as catalyst. The dimer was removed by fractional distillation under reduced pressure. The polymers which were suitable as lubricating oils were found to have the following viscometric properties :—

	Monomer	C ₈ /C ₉	C ₉ /C ₁₀
10	Vk _{210° F.}	7.7 CS	7.7 CS
	Vk _{100° F.}	45.7 CS	44.2 CS
	KVI	135	139
	Pour point	- 86° F.	- 65° F.

The oxidation stability was tested by the procedure described in Example II using 100 parts per million of copper powder, with 1.45% by weight of added 10-benzyl phenothiazine and heating at 175° in an atmosphere of oxygen.

The results obtained were as follows :—

Monomer	C ₈ /C ₉	C ₉ /C ₁₀
t ₆₅₀ (hours)	55	81
t ₁₀₀₀ "	82	116

EXAMPLE VII.

A C₉ urea-extract cracked-wax olefine was polymerised using a catalyst component mole ratio, aluminium triethyl : titanium tetrachloride of 0.5 : 1 and treated with hydrogen using Raney nickel as catalyst as in Example VI. The dimer was removed by fractional distillation under reduced pressure.

The polymer which was suitable as a lubricating oil was shown to have the following viscometric properties :—

35	Vk _{210° F.}	29.7 CS
	Vk _{100° F.}	208 CS
	KVI	136

The oxidation stability was tested by the same procedure as described in Example VI with added 10-benzylphenothiazine and the results obtained were as follows :—

t ₆₅₀	46 hours
t ₁₀₀₀	67 hours

WHAT WE CLAIM IS :—

1. A process for the production of hydrocarbon polymers in which an olefine having in the molecule at least six but not more than twenty-five carbon atoms is polymerised in the presence of a catalyst comprising components A and B (as hereinbefore defined) and the polymer is treated with hydrogen in the presence of a hydrogenation catalyst.

2. A process according to Claim 1 in which the olefine is obtained from the thermal

or catalytic cracking of hydrocarbon feed-stock.

3. A process according to Claim 1 in which the olefine is obtained from the cracking of the raffinate of furfural extraction of heavy catalytically cracked cycle oil.

4. A process according to any one of the preceding claims, in which the olefine is a mixture of olefines having in the molecule at least six but not more than twenty-five carbon atoms.

5. A process according to any one of the preceding claims, in which the olefine contains not more than eighteen carbon atoms in the molecule.

6. A process according to any one of the preceding claims, in which the olefine comprises a straight-chain alpha olefine or a mixture containing a large proportion of straight-chain alpha olefines.

7. A process according to any one of Claims 1 to 5, in which the olefine is one of

the general formula
$$\begin{matrix} R \\ \diagup \\ C = CH_2 \\ \diagdown \\ R_1 \end{matrix}$$
 or a mixture containing a large proportion of such olefines wherein R and R₁ are similar or dissimilar alkyl groups and the catalyst component mole ratio (B : A) is between 0.05 : 1 and 0.9 : 1.

8. A process according to any one of the preceding claims, in which the olefine or olefine mixture is purified by treatment with one of the catalyst components before polymerisation.

9. A process according to any one of Claims 1 to 7, in which the olefine or olefine mixture is purified by treatment with sulphuric acid before polymerisation.

10. A process according to any one of Claims 1 to 6, in which the olefine or olefine mixture is purified by treatment with urea before polymerisation.

11. A process according to Claim 10, in which the urea adduct formed on addition of urea to the olefine in the purification treatment is washed with a substantially water-immiscible solvent before decomposition.

12. A process according to any one of the preceding claims, in which the olefine is further purified by treatment with silica-gel before polymerisation.

13. A process according to any one of the preceding claims, in which the mole ratio of Component A to olefine lies between 0.005 : 1 and 0.1 : 1.

14. A process according to any one of Claims 1 to 6 and 8 to 12, in which the catalyst component mole ratio (B : A) is at least 0.05 : 1 and not more than 20 : 1.

15. A process according to Claim 14, in which the catalyst component mole ratio (B : A) is less than 1 : 1.

16. A process according to Claim 14, in

- which the catalyst component mole ratio (B : A) is at least 1 : 1 and not more than 3 : 1.
17. A process according to any one of the preceding claims, in which the purity of hydrogen is at least 95% by weight.
18. A process according to any one of the preceding claims, in which the pressure of hydrogen is at least 10 atmospheres.
19. A process according to any one of the preceding claims, in which the temperature at which the treatment with hydrogen is carried out is above 50° C.
20. A process according to any one of the preceding claims, in which the hydrogenation catalyst is Raney nickel.
21. A process according to any one of the preceding claims, in which the dimer is removed.
22. A process according to Claim 21, in which the dimer is removed by fractional distillation under reduced pressure.
23. A process according to either of Claims 21 and 22, in which low molecular weight polymer other than dimer is also removed.
24. A process according to any one of the preceding claims, in which Component A comprises an inorganic compound of Groups 4a, 5a or 6a of the Periodic Table.
25. A process according to Claim 24, in which Component A comprises a chloride, bromide or iodide of a metal of Groups 4a or 5a of the Periodic Table.
26. A process according to Claim 25, in which the metal is titanium, zirconium or vanadium.
27. A process according to any one of Claims 1 to 15 and 17 to 26, in which Component A is liquid at normal temperatures and pressures and the catalyst component mole ratio (B : A) is less than 1 : 1.
28. A process according to any one of Claims 1 to 15, 17 to 27 in which the metal present in Component A is in its highest valency state and the catalyst component mole ratio (B : A) is less than 1 : 1.
29. A process according to any one of Claims 24 to 28 in which Component A comprises titanium tetrachloride.
30. A process according to any one of the preceding claims in which Component B comprises either (1) an aluminium trialkyl ; or (2) an aluminium compound of the general formula R_1R_2AlX in which R_1 and R_2 are similar or dissimilar and each represents a hydrogen atom or a hydrocarbon radical and X represents a hydrogen atom, a halogen atom, an alkoxy group or an aryloxy group
- or the residue of a secondary amine or amide, carboxylic acid or sulphonic acid ; or (3) an aluminium compound of the general formula $RAlX_1X_2$ in which R represents a hydrogen atom or a hydrocarbon radical and X_1 and X_2 are similar or dissimilar and each represents a halogen atom, an alkoxy group or an aryloxy group.
31. A process according to Claim 30, in which the alkyl group has less than six carbon atoms.
32. A process according to any one of the preceding claims, in which Component B is aluminium triethyl.
33. A process for the production of hydrocarbon polymers substantially as hereinbefore described with particular reference to the examples.
34. A hydrocarbon polymer produced by a process using a catalyst component mole ratio (B : A) of at least 1 : 1 according to any one of Claims 1 to 6, 8 to 14, 16 to 26 and 29 to 32.
35. A hydrocarbon polymer produced by a process using a catalyst component mole ratio (B : A) of at least 1 : 1 as hereinbefore described with particular reference to Examples 1 and 2.
36. A hydrocarbon polymer produced by a process using a catalyst component mole ratio (B : A) of less than 1 : 1 according to any one of Claims 1 to 15 and 17 to 32.
37. A hydrocarbon polymer produced using a catalyst component mole ratio (B : A) of less than 1 : 1 as hereinbefore described with particular reference to Examples 3 to 7.
38. A hydrocarbon polymer according to either of Claims 34 and 35 containing a minor proportion of antioxidant.
39. A hydrocarbon polymer according to either of Claims 36 and 37 containing a minor proportion of antioxidant.
40. A blend of a polymer according to any one of Claims 34, 35 and 38 with a mineral or synthetic lubricating oil.
41. A blend of a polymer according to any one of Claims 36, 37 and 39 with a mineral or synthetic lubricating oil.
42. A blend of a polymer according to any one of Claims 34, 35 and 38 with a polymer according to any one of Claims 36, 37 and 39.

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